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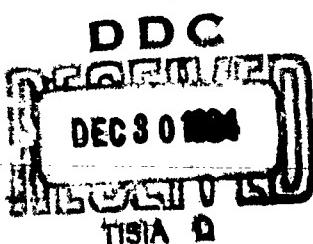
TECHNICAL NOTE No. CPM. 80

THE THERMAL ACCOMMODATION OF HELIUM AND ARGON ON TUNGSTEN AND PLATINUM AT ELEVATED TEMPERATURES

by

W. Watt and R. Moreton

AUGUST 1964



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SUMMARY

The thermal accommodation coefficients of helium and argon have been measured on tungsten at temperatures of 800° - 1512°C under conditions which are considered to give a clean tungsten surface after flashing to 2400°C . Measurements of the accommodation of the same gases and of nitrogen have also been made on platinum at temperatures of 910° - 1320°C .

An accommodation coefficient of 0.018 for helium on tungsten and of 0.24 for argon, both constant over the temperature range studied, was found. On platinum these gases and also nitrogen had constant accommodation coefficients over the range studied, the values being 0.026, 0.38 and 0.34 for helium, argon and nitrogen respectively. The values for helium on tungsten have been compared with those obtained by other workers at temperatures of -170°C to $+58^{\circ}\text{C}$ and reasonable agreement has been found. It is concluded that the thermal accommodation of helium on tungsten is independent of temperature up to 1512°C .

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1 INTRODUCTION

The thermal accommodation of an assembly of gas molecules, characterised by a Maxwell-Boltzmann distribution of energies, impinging on the surface of a solid at a different temperature and rebounding with an exchange of energy is defined in terms of energy fluxes as

$$\alpha = \frac{E - E_0}{E_1 - E_0}$$

where α = thermal accommodation coefficient

E = average energy of the gas molecules leaving the surface

E_0 = average energy of the impinging gas molecules

E_1 = average energy which the gas molecules would carry away if they came into thermal equilibrium with the surface.

The original definition of α by Knudsen¹ was in terms of temperatures, viz.

$$\alpha = \frac{T - T_0}{T_1 - T_0}$$

where T = average temperature of gas molecules leaving the surface, °C

T_0 = average temperature of the impinging gas molecules, °C

T_1 = temperature of the surface, °C.

This definition in terms of temperature is only true if the gas molecules leaving the surface have a Maxwell-Boltzmann energy distribution.

The thermal accommodation coefficient may be of considerable importance in understanding the chemical kinetics of reactions between gases and hot solids. In studies of the kinetics of such reactions it is common practice to use an electrically heated filament in a vessel containing the gas at a pressure of a few microns, the walls of the vessel being at room temperature. In such a system, since the mean free path of the gas molecules is many times the diameter of the filament (e.g. 100-1000 times), the gas molecules impinging on the heated surface are at room temperature as they are in thermal equilibrium with the walls of the vessel and not with the surface of the filament. The rates of reactions obtained under these circumstances are not therefore necessarily the same as when the solid and the gas are at the same temperature. This may be especially true for reactions between graphite and oxidising gases such as oxygen, carbon dioxide and water vapour. These reactions have been studied at low pressures using graphite filaments at 1200° - 2000°C and low reaction probabilities, 1×10^{-4} to 1×10^{-5} , have been obtained with the rate depending to some extent on the previous history of the graphite filament².

The work described in this note was undertaken to gain experience of measuring accommodation coefficients at high temperatures, for the eventual application of the technique to systems involving chemical reactions, i.e. for a better understanding of chemical kinetics in low pressure systems. Very little work has been done on the measurement of accommodation coefficients at elevated temperatures.

It was decided to work initially with a non-reactive system so the accommodation coefficients of the inert gases helium and argon were measured on platinum and tungsten filaments and also nitrogen on platinum. Accommodation coefficient measurements on tungsten at elevated temperatures are of considerable interest to other workers in the Physics Division of C.P.M. Department who are working on accommodation coefficients of gases on tungsten, using a momentum balance to measure the translational energy of the reflected molecules³. Accurate measurements of the accommodation coefficient of helium on tungsten over a wide temperature range would also be of great value to theoretical workers in the field.

The method normally used for measuring accommodation coefficients employs an electrically heated wire along the axis of a cylindrical vessel. The power loss from the wire in vacuo at the operating temperature is measured and then a known pressure of gas admitted. The temperature of the wire, measured by the resistance, is adjusted to that before admission of the gas, and the new power loss from the wire determined. The difference between the two power readings gives the loss to the gas. The gas pressure should be such that free molecule conduction conditions exist.

The classical work of Roberts on the accommodation of helium on tungsten at gas temperatures from 79° to 295°K^{4,5,6} with filament temperatures 10° - 20°C above the gas temperatures showed the need for obtaining a surface free of adsorbed gas and of keeping it clean during the measurements by working with a clean vacuum system and high purity helium. To obtain these conditions the surface was flashed to a high temperature, about 2000°C, to clean it of adsorbed gases then the measurement of power loss in high purity helium was carried out as quickly as possible. Roberts obtained values of 0.025 at 79°K, 0.046 at 195°K and 0.057 at 295°K. Little work has been done on the accommodation coefficients of gases on filaments at 800°C and upwards, the reason being the strong dependence of radiation on temperature so that the power loss to the gas becomes an increasingly small fraction of the radiation loss and the resistance change smaller.

Mann⁷, measured the accommodation of helium, argon, hydrogen and oxygen on platinum at filament temperatures ranging from 100° to 1000°C. In the method employed the filament was one arm of a Kelvin resistance bridge; the resistance and also the potential drop across the filament was measured. Gas was admitted to a known pressure, the bridge rebalanced by increasing the voltage across it and the new power loss determined. Mann found that the accommodation coefficient of helium on platinum at 100°C rose with time after flashing at 1000°C from 0.12 after $\frac{1}{2}$ min to 0.25 after 7 min; this indicates contamination of the surface. At a filament temperature of 1000°C the value was 0.066. Treatment of the filament at 1000°C with oxygen reduced the accommodation coefficient to 0.03 to 0.04. At temperatures of 100° to 800°C a variation of α with time interval from cleaning with oxygen at 1000°C was noted, but the

values obtained by extrapolating to zero time interval converged to a common value of about 0.04. Mann concludes by saying that the variation of α with temperature is small provided the condition of the surface is kept unaltered.

Thomas and Schofield⁸ report measurements of the accommodation coefficient of helium on tungsten over the temperature range -190° to +30°C with filament temperatures of -170° to +47°C. They used an evaporated film of aluminium in the filament vessel as a "getter" and obtained values for α of 0.015 to 0.017 with virtually no temperature coefficient.

Wachmann⁹ has studied the accommodation coefficient of helium on tungsten with and without the presence of adsorbed gas on the tungsten surface. Clean conditions were obtained by the presence of an evaporated layer of misch metal on the walls of the filament vessel to act as a "getter" for the reactive gases. Filament temperatures of 58°C and wall temperatures of 31.7°C were used. On a clean tungsten surface under these conditions helium was found to have an accommodation coefficient of 0.020. Measurements with adsorbed oxygen on the tungsten showed three or possibly four types of films corresponding to helium accommodation coefficients of 0.065, 0.085, 0.107 and 0.185.

Moyer and Gomer¹⁰ worked on the energy exchange between the noble gases and heated graphite filaments at temperatures from 852° to 1502°C. Again the filament formed one arm of a resistance bridge. The out-of-balance D.C. voltage produced on admission of the gas was chopped at 400 cycles/second, amplified, rectified, and used to drive an amplifier supplying part of the filament heating current. This was used to rebalance the bridge by increasing the heating current to restore the filament to the original temperature. The current increase Δi was measured. In this method the power radiated was kept constant and the loss Q due to free molecule conduction is given by $Q = 2Ri \Delta i$ watts where R is the resistance of the filament and i is the current passed.

They worked with helium, hydrogen, neon, krypton and methane and found in all cases that the power loss due to the gas was independent of filament temperature at any given wall temperature below a certain critical temperature which was different for each gas. An accommodation mechanism of temporary adsorption followed by evaporation at a constant temperature appreciably below the filament temperature was postulated. When the wall of the filament vessel was raised above this evaporation temperature the power loss to the gas became proportional to the temperature difference between filament and wall.

De Poorter and Scarcey¹¹ presented the first work on the accommodation coefficients of various gases on tungsten at elevated temperatures by the classical method of measuring power loss. They measured the increase in current when the gas was admitted and from it calculated the power loss to the gas. The background pressure in their apparatus is given as 6×10^{-6} mm Hg, and they state that this implies an oxygen covered surface. No reliable results for helium are given; for neon they report an accommodation coefficient of 0.274 at a filament temperature of 1607°C falling to 0.236 at 1847°C, and for argon a value of 0.455 at 1587°C falling to 0.349 at 2062°C. The power loss to the gas was approximately constant over these temperature ranges and it is concluded that, as Meyer and Gomer postulate for neon and argon on graphite, a mechanism of temporary adsorption followed by evaporation at a constant temperature exists.

2 EXPERIMENTAL2.1 Theory of the method used

In the method used in this work the filament formed one arm of a Kelvin resistance bridge used under constant voltage conditions. Potential leads were taken from a central uniform temperature zone of the filament to the bridge, which was balanced in vacuo with the filament at the desired temperature; the resistance change on admitting the gas was measured by noting the out of balance deflection of the bridge galvanometer.

It can be shown¹² that the power loss to the gas under constant voltage conditions is given by

$$H = 4 \epsilon_i A \sigma T^3 \frac{dT}{dR} \Delta R + \frac{V^2}{R^2} \Delta R \quad (1)$$

where H = power loss to the gas from the filament, watts

$\frac{V^2}{R}$ = the power input to the filament between the potential leads at a filament temperature of $T^{\circ}\text{K}$

V = voltage between potential leads, volts

R = resistance between potential leads, ohms

ϵ_i = total emissivity of the filament at $T^{\circ}\text{K}$

A = surface area of the filament, cm^2

σ = Stefan-Boltzmann constant, watts $\text{cm}^{-2}\text{K}^{-4}$.

The assumptions in deriving this expression are

- (1) no change in the volts across the filament on admission of the gas
- (2) the drop in temperature of the filament is small, i.e.

$$\frac{\Delta T}{\Delta R} = \frac{dT}{dR}$$

ΔT = temperature drop of filament, $^{\circ}\text{K}$

ΔR = resistance change of the filament, ohms

$\frac{dT}{dR}$ = reciprocal of the temperature coefficient of resistance of the filament at $T^{\circ}\text{K}$, $\text{K} \text{ohm}^{-1}$

- (3) the presence of the gas does not change the total emissivity of the filament.

The first term on the right is the change in the watts radiated by the filament as a result of the temperature drop ΔT while the second term on the right is the change in the power used by the filament as a result of the resistance change. Since the voltage does not change the resistance drop causes a small increase in the power consumed by the filament so that the change in the watts radiated must be corrected by this amount.

The change in the watts radiated is directly proportional to the total emissivity so that equation (1) used as it stands requires an accurate value for this constant at each temperature used. This can be obviated by constructing a watts versus resistance curve for each filament in vacuo and finding dW/dR from this curve at the desired temperatures. Equation (1) used in this form becomes

$$H = \Delta R \left\{ \frac{dW}{dR} + \frac{V^2}{R^2} \right\} \quad (2)$$

This assumes that all the power is lost by radiation or gaseous conduction, i.e., the end cooling is negligible. Finally α the thermal accommodation coefficient is calculated using the equation

$$\alpha = \frac{H}{A z \left(C_v + \frac{R}{2} \right) J(T_f - T_w)}$$

where A = surface area of filament, cm^2

z = number of moles of gas striking 1 cm^2 of surface per second

C_v = specific heat of the gas at constant volume at the temperature of the filament, cals mole $^{-1}$ $^{\circ}\text{C}^{-1}$

R = gas constant, cals mole $^{-1}$ $^{\circ}\text{C}^{-1}$

J = mechanical equivalent of heat, joule cal $^{-1}$

$(T_f - T_w)$ = temperature difference between the filament at T_f $^{\circ}\text{C}$ and glass wall at T_w $^{\circ}\text{C}$.

The term $\frac{R}{2}$ is necessary to make allowance for the fact that the translational molar heat capacity of a molecular stream of gas molecules is greater than the corresponding quantity for a still gas.

The number of moles of the gas striking 1 cm^2 of filament surface per second, z , was calculated using the following expression derived from kinetic theory.

$$z = \frac{3.537 \times 10^{19} p}{N (MT)^{\frac{3}{2}}}$$

where p = gas pressure, microns

M = molecular weight of the gas

T = temperature of the impinging molecules

N = Avogadro's number.

2.2 Apparatus

The Pyrex glass apparatus is shown diagrammatically in Fig. 1. The vessel (1) 5 cm dia, 33 cm long, containing the filament (2) was connected on one side via a liquid nitrogen trap to a conventional pumping system of backing pump and oil diffusion pump and on the other side to a gas storage and measuring system (3) evacuated on the same pumping system. The taps T_1 and T_2 were lubricated

with Apiezon L grease* and also the cone and socket joints (12). The gas storage vessel (3) was connected via a needle valve (6) to a glass bulb (7) containing the test gas so that a few microns pressure of gas could conveniently be admitted. The pressure of the gas after sharing with the filament vessel by opening tap T_2 was measured by the McLeod gauge attached to the storage vessel. This was a constant compression McLeod gauge reading to ± 0.025 microns pressure. A liquid nitrogen trap was in the line between the gas storage vessel and the McLeod gauge. Both the filament and gas storage vessels had appendices cooled in liquid nitrogen for the experiments with the platinum filament. During experiments with the tungsten filament, done after those with platinum, the appendix on the gas storage vessel was replaced by a flask containing outgassed charcoal, cooled in liquid nitrogen, 11. Ultimate pressures in both vessels were read with ionisation gauges, I.G.1 and I.G.2. The Pt. filament was gripped by small steel pin chucks (4) which were screwed and bolted into water cooled copper blocks (5); the copper tubes (8) for the water cooling were also the current conductors and were sheathed in glass tubing so that they could be used as guides for the leads to the potential contacts (9) on the filament. The platinum was 0.40 mm diameter of total length between the pin chucks 20.4 cm. The potential leads were of 0.1 mm platinum wire, 5 cm long, spot welded to the filament and 12.30 cm apart.

The other ends of the potential leads were welded to 0.4 mm platinum wires led out of the filament vessel through copper capillary tubing soldered into housekeeper seals (10).

The tungsten filament was held differently. After electrolytic polishing in 40% NaOH solution it was 0.46 mm diameter and was spot welded to 2 mm diameter molybdenum rods which had been brazed into stainless steel rods with 2 BA threads and screwed into the copper blocks, as were the pin chucks. This mounting method was used as it was desired to age the filament at high temperatures and to flash it at 2400°C for cleaning before each measurement. The potential leads were of 0.1 mm tungsten wire about 5 cm long spot welded to the filament and to 0.4 mm platinum wires led out of the vessel as for the platinum filament. The total length of the filament was 21.47 cm and the potential leads were 10.99 cm apart.

* The vapour pressure of Apiezon L grease is given by the manufacturers as 10^{-10} to 10^{-11} mm Hg at room temperature.

The power for heating the filaments was obtained from a transistorised D.C. power unit with a stepless variable output. An electronic voltage stabiliser with a fast response time in the input side of the power unit gave satisfactory voltage stability.

The Kelvin bridge could be read to 1×10^{-4} ohms, and the bridge galvanometer was a Sefram Graphispot. This contained a pen recorder locked to the light beam from the galvanometer so that a trace of the out of balance bridge current against time could be obtained.

2.3 Experimental procedure

Since the procedures with the platinum and tungsten filaments were slightly different they are described separately.

Platinum filament

The temperature distribution along the length of the filament and the watts/resistance characteristics were measured by heating to different temperatures in vacuo. The resistance between the potential leads was measured with the Kelvin bridge and also calculated from the voltage dropped between the potential leads and the current through the filament; the voltage was measured by a potentiometer to ± 0.1 mV and the current to ± 0.1 mA from the voltage drop across a 0.1 ohm standard resistance in series with the filament. The two resistance values agreed to within 0.1 percent. The temperature was measured with an optical pyrometer, calibrated against an N.P.L. standard lamp, and the readings corrected for spectral emissivity using the values given by Goldsmith, Waterman and Hirschorn¹⁵. Values of dW/dR were computed from the data for the temperatures 910°, 1100°, 1320° and 1500°C.

For an experiment the filament was set to the required temperature using the resistance temperature data, and the optical temperature checked. All this was done in vacuo with the filament vessel open to the pumps and with the cold trap and appendix of the filament vessel (13) cooled in liquid N₂. The background pressure in the apparatus was 2×10^{-6} mm with no measurable degas rate over a period of one hour after isolating from the pumps. The bridge was balanced and the requisite amount of test gas admitted to the storage side. The chart drive of the recording galvanometer was started and a calibration deflection of a 1×10^{-4} ohm change was made on the Kelvin bridge. Tap T₁ to the pump was closed and T₂, the gas sharing tap, opened about one second afterwards. The deflection due to the resistance change of the filament was completed in about five seconds, and after about one minute T₂ was closed and T₁ opened to the pumps. The pressure in the gas storage vessel was then read, this being the pressure in the two sides of the apparatus after admission of the gas to the filament vessel.

After experiments with helium on the platinum with no pretreatment, measurements were made after treating the filament while at 1320°C in a stream of oxygen at one micron pressure, the flow being controlled by the needle valve. After 10 minutes of this treatment the flow was stopped, the oxygen pumped out, and the filament set at the required temperature if different from 1320°C. Then the test gas, which had been admitted to the gas storage vessel, was shared with

the filament vessel, after the trace of the bridge galvanometer had become stable. This took about five minutes. This oxygen treatment was done as it was suspected that carbon contamination of the filament was occurring.

A typical resistance change trace for argon on the platinum filament is shown in Fig. 2.

Tungsten filament

In working with tungsten it is necessary to be able to flash the filament to about 2400°C to remove the chemisorbed oxygen which has a heat of adsorption of 180 Kcals mole $^{-1}$ for a complete monolayer¹⁴, corresponding to a heat of desorption as oxygen atoms of 148 Kcal gram-atom $^{-1}$. A double pole double throw switch was inserted in the external leads to the filament so that it could be connected to the stabilised power supply or to a D.C. rectifier capable of giving enough power to heat the filament to 2400°C . The apparatus was also dismantled and baked in air to 450°C before putting in the tungsten filament, which was then heated in vacuo at 2000°C to age it and thus stabilise its resistance. During this ageing the vacuum slowly improved probably due to degassing of the glass and finally became steady at 2×10^{-7} mm with all liquid nitrogen traps on. It was found that with the filament cold and the apparatus isolated from the pumps the pressure rose to about 1×10^{-5} mm overnight. No runs were done on any day until with the filament on at 2000°C and all liquid nitrogen traps on the pressure went down to 2×10^{-7} mm.

Because of the presence of the greased traps and cone and socket joints (12) thorough baking out of the assembled apparatus was not possible.

From the analysis of the gases used (see section on purity of materials) it was considered necessary to purify them before admission to the tungsten filament by exposing them to charcoal at liquid nitrogen temperature. A flask containing charcoal (11) previously outgassed at 1500°C for 24 hours to a pressure of 10 microns was attached to the gas storage vessel. The helium or argon was exposed to charcoal at liquid nitrogen temperature for at least ten minutes. Tests with oxygen and nitrogen at a few microns pressure showed that 86 percent of these gases were adsorbed by the charcoal under these conditions.

The best flashing procedure for cleaning the tungsten was found to be flashing at 2400°C for 15 second periods at $\frac{1}{2}$ minute intervals until two successive flashes gave no observable pressure rise from 2×10^{-7} mm. Two or three flashes sufficed. Longer flashes caused the pressure to rise unduly e.g. a two minutes flash caused a pressure rise to about 2×10^{-6} mm, this being considered due to the rest of the apparatus warming up and disengaging gas. The test gas was admitted after about 3 minutes when the resistance had stabilised after the last flash. A typical galvanometer trace showing the resistance change at a filament temperature of 1062° on admission of helium is shown in Fig. 3. The upper temperature for measuring α on the tungsten filament in the apparatus as described was found to be around 1512°C . A resistance change trace at this temperature is shown in Fig. 4. It can be seen that after the initial rapid resistance drop on admission of the gas there is a slower rise and the reverse occurs on pumping out. It was found that the secondary effect was due to a slight resistance change in the long current conductors to the bottom of the filament. These were heated by radiation from the filament and admission of

the gas cooled them slightly and comparatively slowly causing a slight resistance drop and hence more current through the filament. At temperatures of about 1700°C the effect was very marked the secondary resistance change being greater than the original cooling change.

2.4 Purity of materials

The platinum wire used was of Thermopure quality, given as 99,999% purity.

The tungsten wire was analysed after electropolishing and the analysis was:-

Impurity	Impurity content Atomic percent
Carbon	0.10
Iron	0.18
Thorium	Nil

The gases used were ex cylinders, the stated impurity contents being as follows

	Impurity content, ppm by volume		
	Helium	Argon	Nitrogen
H ₂ O	6	-	-
H ₂	1	0.5	1
Ne	30	-	1
O ₂	25	5	10
N ₂	30	40	
CO ₂	6	5	5

After exposure to the charcoal at liquid nitrogen temperature the impurity contents were estimated to be

	Impurity content, ppm by volume	
	Helium	Argon
H ₂ O	Nil	Nil
H ₂	not estimated	not estimated
Ne	not estimated	not estimated
O ₂	3.0	0.8
N ₂	5.0	6.6
CO ₂	Nil	Nil

These estimates are based on measured adsorptions of oxygen and nitrogen in the apparatus with the charcoal as subsequently used, assuming the most pessimistic case, viz. that at partial pressures of oxygen and nitrogen of about 1×10^{-4} microns the amount adsorbed on the charcoal is proportional to the pressure.

2.5 Accuracy

Temperature was read to $\pm 5^{\circ}\text{C}$ on an optical pyrometer which had been calibrated against a standard N.P.L. lamp. The temperatures were corrected for the spectral emissivities of tungsten and platinum using the data given by Goldsmith, Waterman and Hirschorn¹³. The measurements of filament area and dW/dR are estimated to be $\pm 2\%$ and $\pm 3\%$ respectively.

The accuracy of the measurements of the resistance changes vary with the temperature, since the changes were smaller at the higher temperatures and also varied with the gases used, because of the differences in the accommodation coefficients of the gases. After allowing for the errors in reading the galvanometer deflections the overall accuracy of the accommodation coefficients on tungsten is estimated as follows

Filament temperature $^{\circ}\text{C}$	Accuracy of thermal accommodation coefficient, percent, for	
	Holium	Argon
800	± 7.0	± 5.5
1062	± 8.5	± 6.0
1285	± 10.0	± 6.5
1512	± 12.0	± 7.0

The errors for the accommodation coefficients of helium on platinum are about 1% less and those for the argon and nitrogen on platinum about 0.5% less than those on tungsten. No corrections were made for the variation of the temperature of the wall of the filament vessel. It was measured with a contact thermocouple at each filament temperature but the corrections to the calculated accommodation coefficients were all less than 0.5% and so were ignored.

The temperature of the impinging gas molecules was taken as 30°C in calculating the accommodation coefficients.

3 RESULTS

3.1 General

In all cases the power loss to the gas at each filament temperature was measured with several different gas pressures up to about five microns and the power loss was always found to be proportional to the gas pressure. The best straight line was drawn through the experimental points and from this the power loss in watts cm^{-2} micron $^{-1}$ was estimated and the accommodation coefficient calculated from this value.

3.2 Platinum filament

The results for the power loss in helium of the platinum filament without any pretreatment in oxygen are shown graphically in Fig. 5 and the derived accommodation coefficients are given in Table 1. There is a large drop in the α in going from 1320° to 1500°C filament temperature. It seems that the surface of the filament has been cleaned up at the higher temperature. Carbon contamination from grease or oil vapours was suspected at the lower temperatures; this may have been cleaned up and the surface kept clean by evaporation of platinum at 1500°C. A slight darkening of the walls of the filament vessel was observed after the runs at 1500°C. Because of this no further runs were done at this temperature and the power loss measurements at the lower temperatures were repeated, after the filament had been heated at 1320°C for 10 min in a stream of oxygen at about 1.0 micron pressure before each power loss run.

Fig. 6 gives the power loss against pressure for helium and argon after cleaning the filament in the above manner and the accommodation coefficients are given in table 1 which includes the results for nitrogen, also on oxygen cleaned platinum.

The accommodation coefficients are all lower than those found with the untreated platinum and are independent of the filament temperature.

3.3 Tungsten filament

The results for the power losses from tungsten to helium and argon, flashed to 2400°C before each experiment, are shown graphically in Figs. 7 and 8 and the derived accommodation coefficients are given in Table 2. No experiments were done with nitrogen on tungsten because a chemisorbed layer would be formed at the temperatures used in the experiments.

4 DISCUSSION

In any accommodation coefficient measurements with tungsten the first question one must ask is what is the degree of cleanliness of the surface, that is, what is the extent of surface coverage with adsorbed oxygen nitrogen and carbon-monoxide? In this work there is no doubt that with a background pressure of 2×10^{-7} mm and a flashing temperature of 2400°C the surface should be cleaned of nitrogen and carbon monoxide. Carpontor, Humphries and Mair¹⁵ have calculated that at a filament temperature of 2700°K and for a surface coverage of 10^{-2} the equilibrium pressure for CO is 2×10^{-4} mm, for N₂ it is 8×10^{-4} mm, but for O₂ with 0.1 surface coverage it is 4×10^{-7} mm. This pressure is only twice the background pressure obtained in these experiments.

Fig. 9 shows that there is only a small change in the accommodation coefficient on increasing the time interval between flashing and admission of helium. If the residual gases had contained appreciable oxygen then the α would have increased markedly; for example a measurement at 1062°C with no flashing on pumping out the apparatus after standing overnight cold gave an α of 0.11.

The filament after use was examined for any preferred crystal orientation by X-ray diffraction and it was found that the 110 plane had a preferred

orientation; an angle of only a few degrees was found between the [110] direction and the wire axis. Microscopic examination of the surface showed equiaxed crystals about 10^{-1} mm diameter, with some thermal etching of the grain boundaries, Fig. 10. Calculations were made of the fractional coverage of the surface assuming adsorption as atoms of all the residual oxygen and nitrogen remaining in the helium after exposure to the charcoal. The number of W atoms available was taken as 14.24×10^{14} per cm^2 for the 110 plane¹⁶. The results were coverages of 5×10^{-5} for oxygen atoms and 1.3×10^{-4} for nitrogen atoms, a total coverage of only 1.8×10^{-4} . Therefore it may be assumed that the energy exchange for helium on tungsten under our conditions is virtually that for a clean tungsten surface.

The coverage from the oxygen and nitrogen in the argon is almost identical to that from the residual helium impurities. The results for the accommodation coefficients of helium on tungsten show two striking features. Firstly the very low values and secondly the fact that the value is independent of temperature, over the range investigated $800^\circ - 1512^\circ\text{C}$. The value of 0.018 obtained should be compared with that obtained by Wachmann, viz. 0.020 for a filament temperature of 58°C and the results of Thomas and Schofield, viz. 0.015 - 0.017.

The following table brings all these results together

Comparison of α of He on W at different temperatures			
	Gas temperature $^\circ\text{C}$	Filament temperature $^\circ\text{C}$	α
Thomas and Schofield	-190	-170	0.015
	-135	-117	0.016
	-80	-62	0.016
	-30	-14	0.017
	+30	+47	0.017
Wachmann	+31.7	58	0.020
Present work	about 30	800	0.018
	"	1062	0.018
	"	1285	0.018
	"	1512	0.018

These results indicate that the α is about 0.018 over a temperature range of -190° to 1512°C and this is true for small or large temperature differences between the tungsten and the helium.

De Poorter and Scaroy¹¹ report one result for helium, an α of 0.179 at a filament temperature of 1597°C . This is about ten times the result obtained in this work at 1512°C . The results of these workers for argon on tungsten are compared with the results of this work in the following table.

Filament temperature °C	Thermal accommodation coefficient A/W	Average temperature of gas molecules leaving the surface °C
This work	800	0.25
	1062	0.25
	1285	0.22
	1512	0.23
De Poorter and Searcy	1587	0.455
	1847	0.390
	1967	0.365
	2062	0.349

The average temperature at which the argon atoms leave the surface calculated by De Poorter and Searcy is close to the lowest filament temperature used in this work (800°C). The mean evaporation temperature 719°C should give an α of 0.89 if the concept of a constant evaporation temperature holds, but in fact an α of 0.25 was found. De Poorter and Searcy admit that their tungsten surface was contaminated with oxygen under their experimental conditions. It may be that a constant evaporation temperature of the argon is characteristic for a surface contaminated with adsorbed oxygen but the present work indicates that it is not the case for a clean tungsten surface.

Fig. 11 is a plot of the power loss against filament temperature for helium and argon and can be interpreted as indicating a direct proportionality between evaporation temperature of the gas atoms and the temperature difference between the filament and impinging gas.

The results with the platinum filament show the same trend as those with tungsten, viz. constant α , and power loss proportional to filament temperature, see Table 1 and Fig. 12. The α values are higher than those obtained on tungsten although the atomic mass ratio gas/metal is almost the same in both cases. The values for helium on platinum, 0.026, are close to the value found by Mann⁷, viz. 0.030 and his observation that the variation of α with temperature is small is fully substantiated in this work. On the other hand he found an α for argon of 0.36 at 1000°C (present work 0.38) rising to 0.50 at 200°C indicating a dependence of α on temperature for argon. It is possible that the higher values found at the lower temperatures could be due to impurities in the argon he used, contaminating the surface. The purity is given as 99.5%, the impurities not being stated.

Diatomie nitrogen behaved like helium and argon on platinum in showing a constant α over the temperature range with a power loss proportional to the filament temperature. The calculated power losses assuming complete accommodation for translational energy are 1.8 times the experimental power losses at the different temperatures. Therefore since the thermal accommodation of the nitrogen is less than that corresponding to complete accommodation for

translational energy no conclusions can be drawn regarding the participation of the internal degrees of freedom in the energy exchange process. It is odd that the accommodation coefficient is independent of temperature. This could mean that the accommodation process does not change with temperature.

The outstanding feature of the results obtained in this work is that the monatomic gases helium and argon have accommodation coefficients on tungsten and platinum which are independent of temperature. The actual values however are not independent of the nature of the solid being greater on platinum than on tungsten. There are some grounds for expecting a higher accommodation coefficient on platinum. Goodman¹⁷ has calculated from theoretical considerations an α for He/W of 0.018 and for He/Pt an α of 0.037, at a gas temperature of 300°K.

The influence of the mass of the impinging gas atoms is shown by considering the ratios $\frac{\alpha A/W}{\alpha He/W}$ and $\frac{\alpha A/Pt}{\alpha He/Pt}$, the figures being 13.2 and 14.4 respectively. If the accommodation coefficients were directly proportional to the mass of the gas atom the ratio should be 10. It would be of interest to do a series of measurements with the other inert gases to investigate this more fully.

5 CONCLUSIONS

(1) A method is described for measuring the thermal accommodation coefficients of helium and argon on tungsten at temperatures of 800° - 1512°, after flashing at 2400°C, and of helium, argon and nitrogen on platinum at 910° - 1320°.

(2) The accommodation coefficient of helium on tungsten was found to be constant at 0.018 over the temperature range 800° - 1512°.

(3) The accommodation coefficient of argon on tungsten over the temperature range 800° - 1512° was found to be nearly constant at a mean value of 0.24.

(4) On platinum, cleaned in one micron pressure of oxygen at 1320°C, helium, argon and nitrogen all show constant accommodation coefficients of 0.026, 0.38 and 0.34 respectively over the temperature range 910° - 1320°.

(5) The accommodation coefficient is not independent of the nature of the solid as the results on platinum are higher than those on tungsten. Nevertheless the ratio of the accommodation coefficients of helium and argon on tungsten is close to the ratio on platinum.

6 ACKNOWLEDGEMENTS

We thank Mr. L. G. Carpenter for his interest in this work and Mr. D. Clark who examined the structure of the tungsten filament by X-ray diffraction.

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TABLE 1

Power losses and accommodation coefficients of helium, argon and nitrogen on platinum at different temperatures

Gas	Filament temperature °C	Pretreatment of filament	Power loss watts cm ⁻² micron ⁻¹ × 10 ²	Accommodation coefficient
Helium	910	None	0.41	0.17
	1100	None	0.48	0.16
	1320	None	0.56	0.16
	1500	None	0.13	0.032
	910	Cleaned in oxygen*	0.065	0.026
	1100	" "	0.085	0.027
	1320	" "	0.095	0.026
Argon	910	Cleaned in oxygen	0.30	0.38
	1100	" "	0.36	0.38
	1320	" "	0.43	0.38
Nitrogen	910	Cleaned in oxygen	0.51	0.34
	1100	" "	0.61	0.34
	1320	" "	0.75	0.33

* Cleaned in oxygen indicates that the filament was heated at 1320°C for 10 minutes while oxygen at one micron pressure was passed over it.

TABLE 2

Power losses and accommodation coefficients of helium and argon
on tungsten at different temperatures

Gas	Filament temperature	Power loss watts cm^{-2} micron $^{-1}$ $\times 10^2$	α
Helium	800	0.038	0.018
	1062	0.052	0.018
	1285	0.061	0.018
	1512	0.073	0.018
Argon	800	0.167	0.25
	1062	0.228	0.25
	1285	0.242	0.22
	1512	0.302	0.23

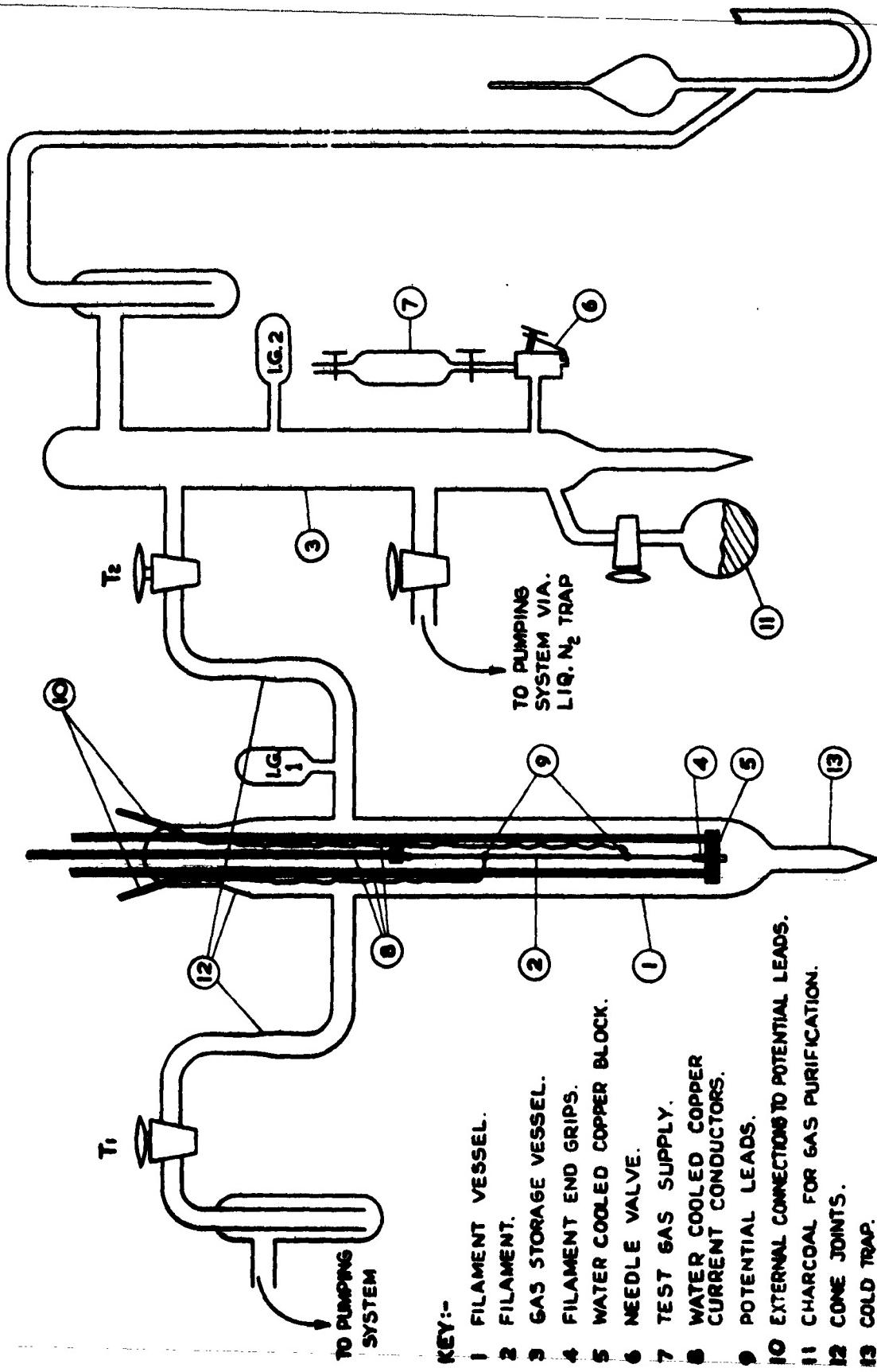


FIG. I. ACCOMMODATION COEFFICIENT APPARATUS.
FILAMENT VESSEL, GAS STORAGE AND MEASURING APPARATUS.

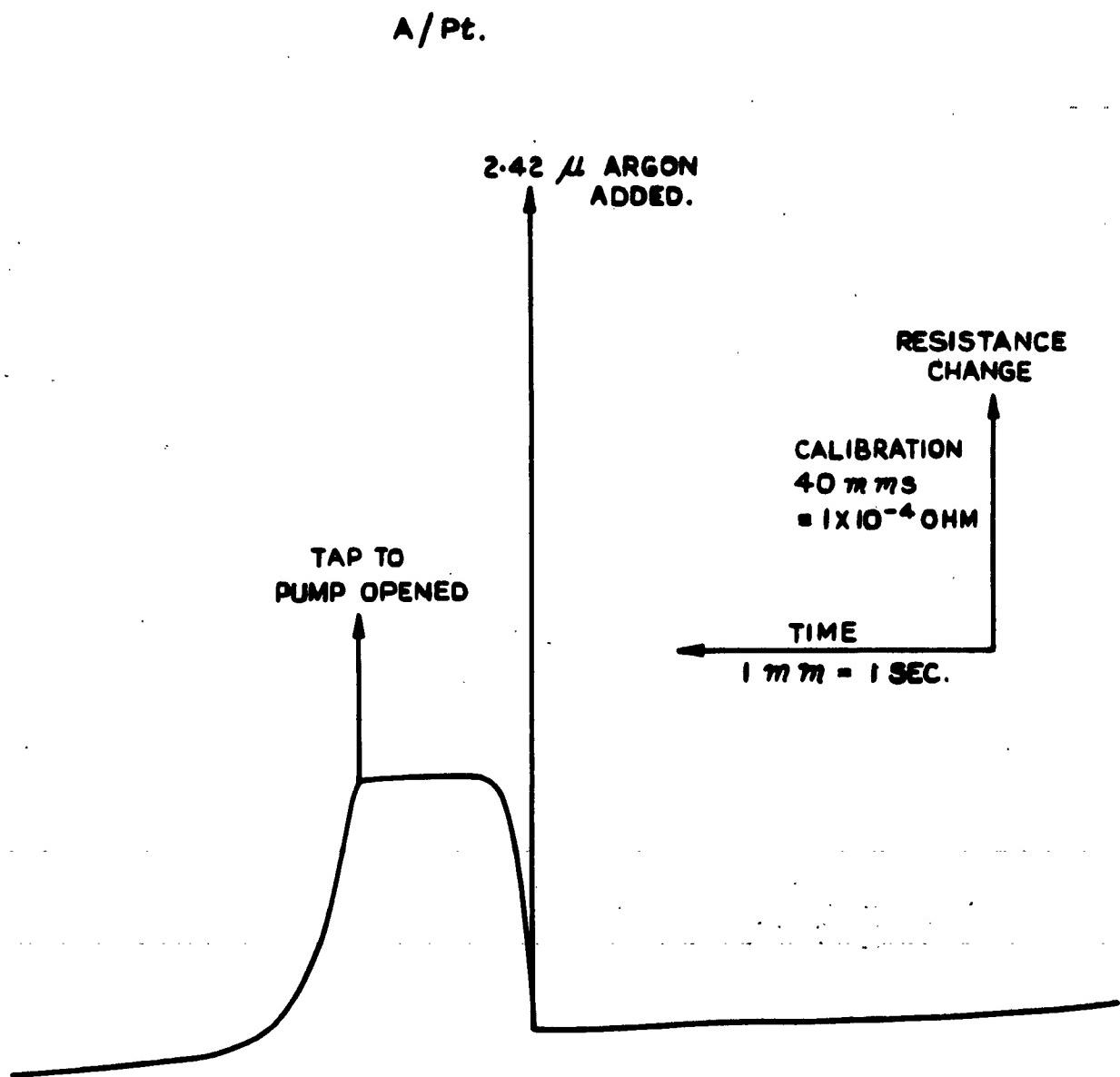


FIG. 2 GRAPHISOT TRACE SHOWING RESISTANCE CHANGE
DUE TO ARGON ON PLATINUM AT T_f 1320°C

He/W

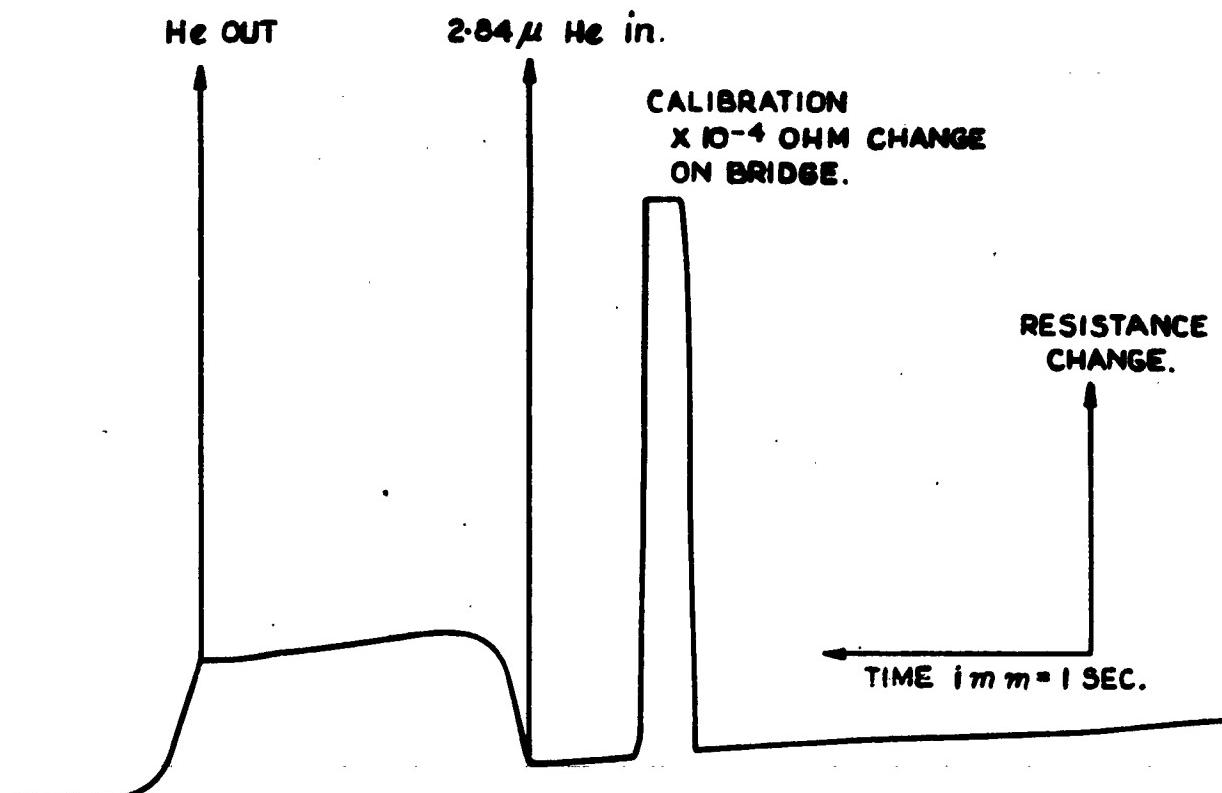


FIG.3 GRAPHISPORT TRACE SHOWING RESISTANCE CHANGE DUE TO HELIUM ON TUNGSTEN T, 1062°C.

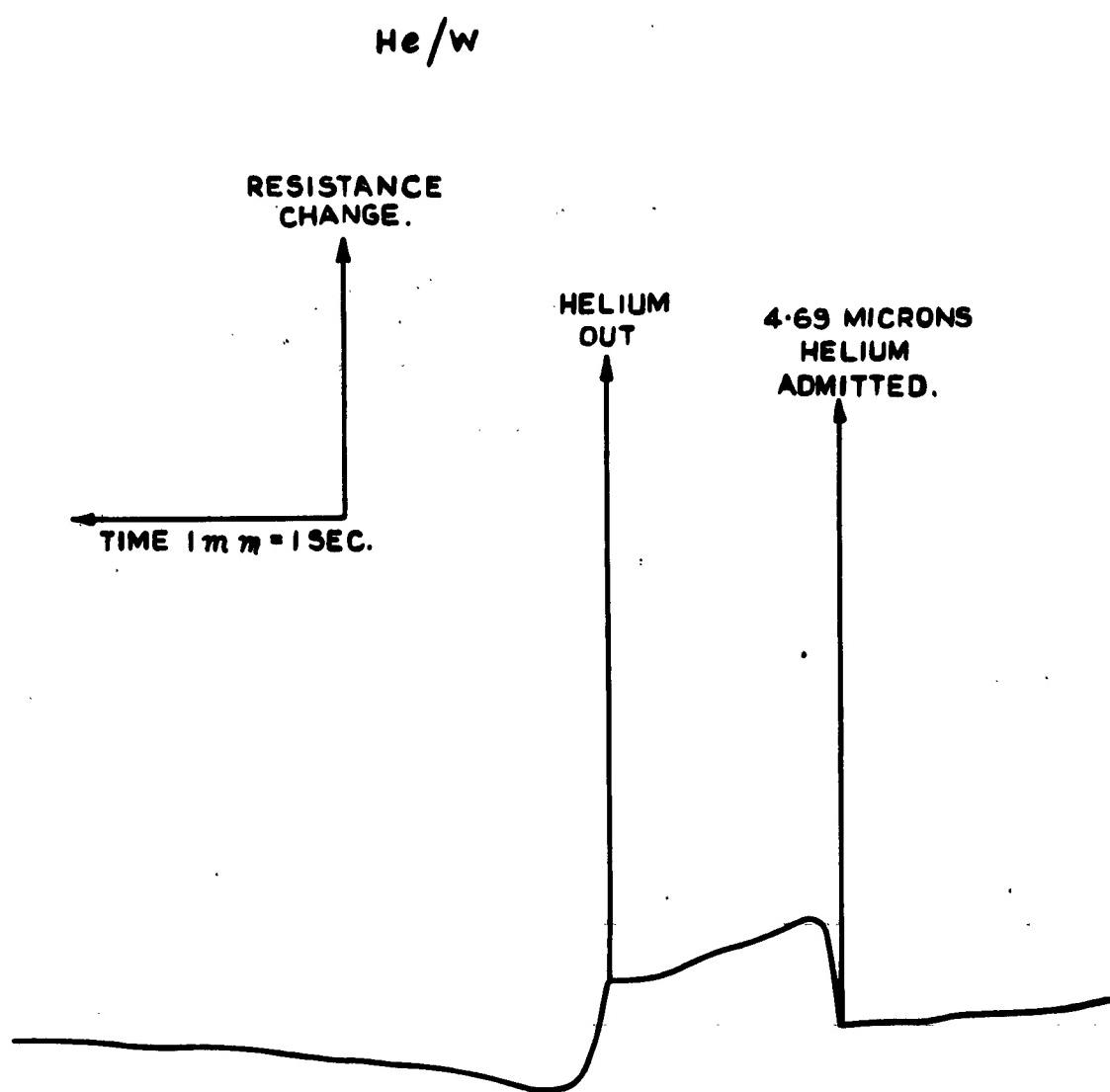


FIG.4. RESISTANCE CHANGE TRACE.
HELIUM ON TUNGSTEN AT FILAMENT TEMPERATURE 1512 °C.
HELIUM PRESSURE 4.69 MICRONS.

HELIUM/PLATINUM (NOT CLEANED)

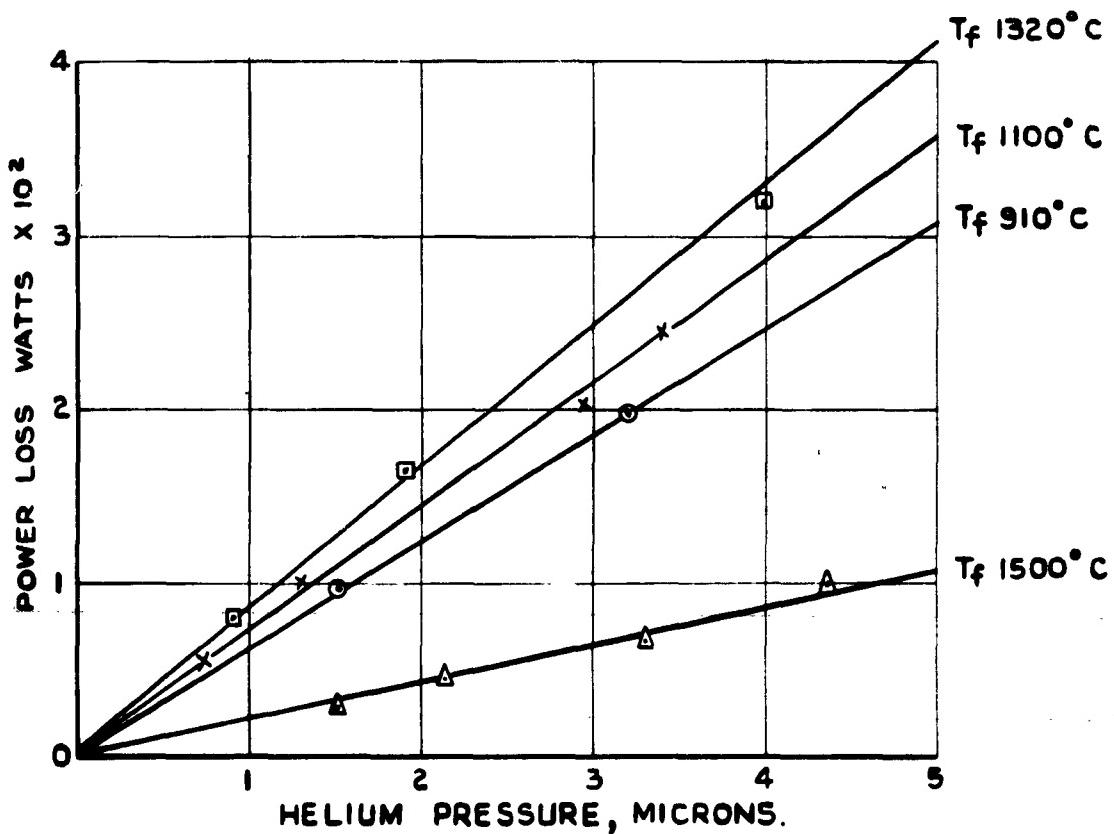


FIG 5 RELATION BETWEEN POWER LOSS AND GAS PRESSURE FOR HELIUM ON PLATINUM AT FILAMENT TEMPERATURES OF 910°, 1100°, 1320° AND 1500°C. NO PRETREATMENT OF FILAMENT.

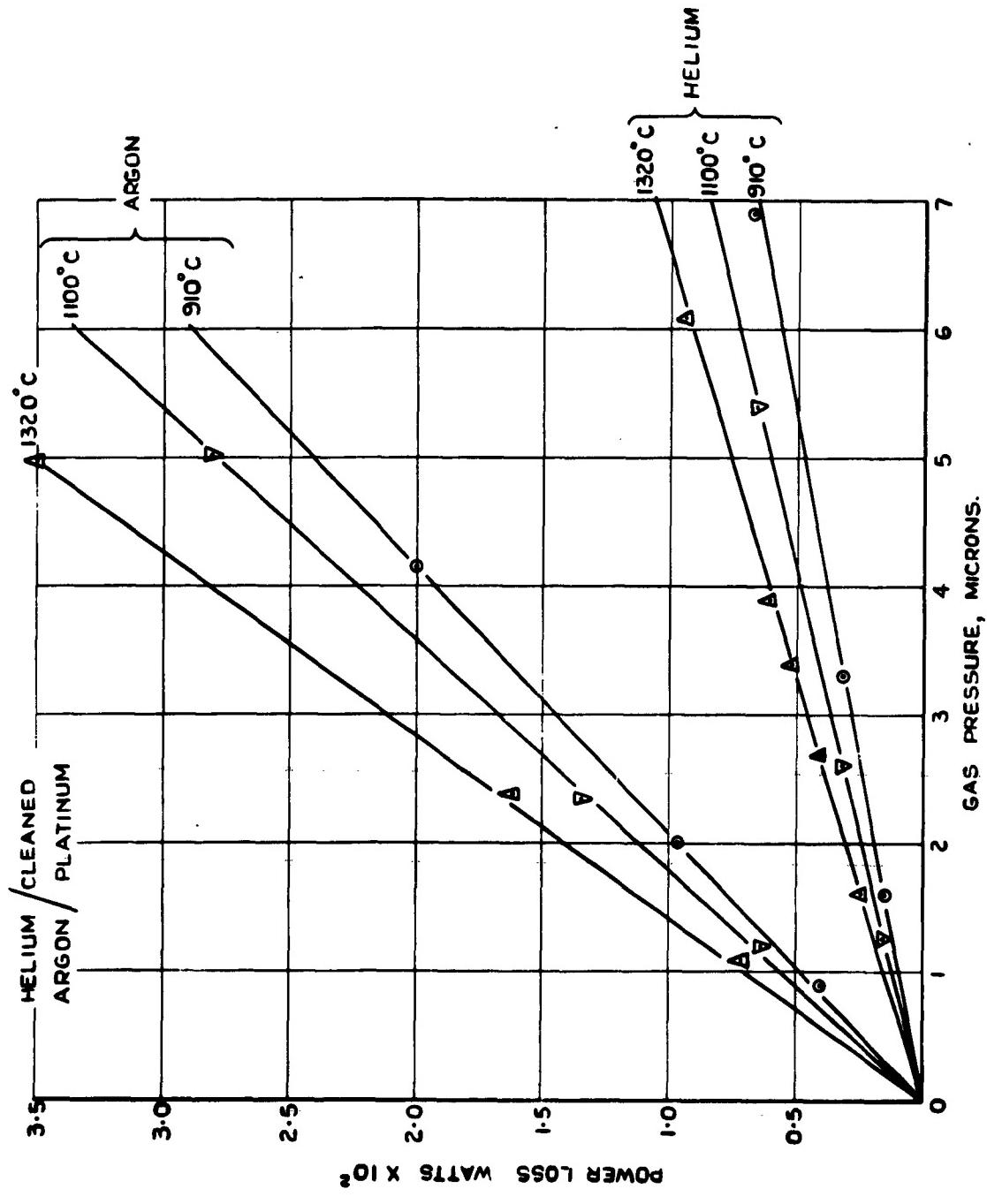


FIG.6 RELATION BETWEEN POWER LOSS AND GAS PRESSURE FOR HELIUM AND ARGON ON PLATINUM AT DIFFERENT TEMPERATURES AFTER TREATMENT IN OXYGEN.

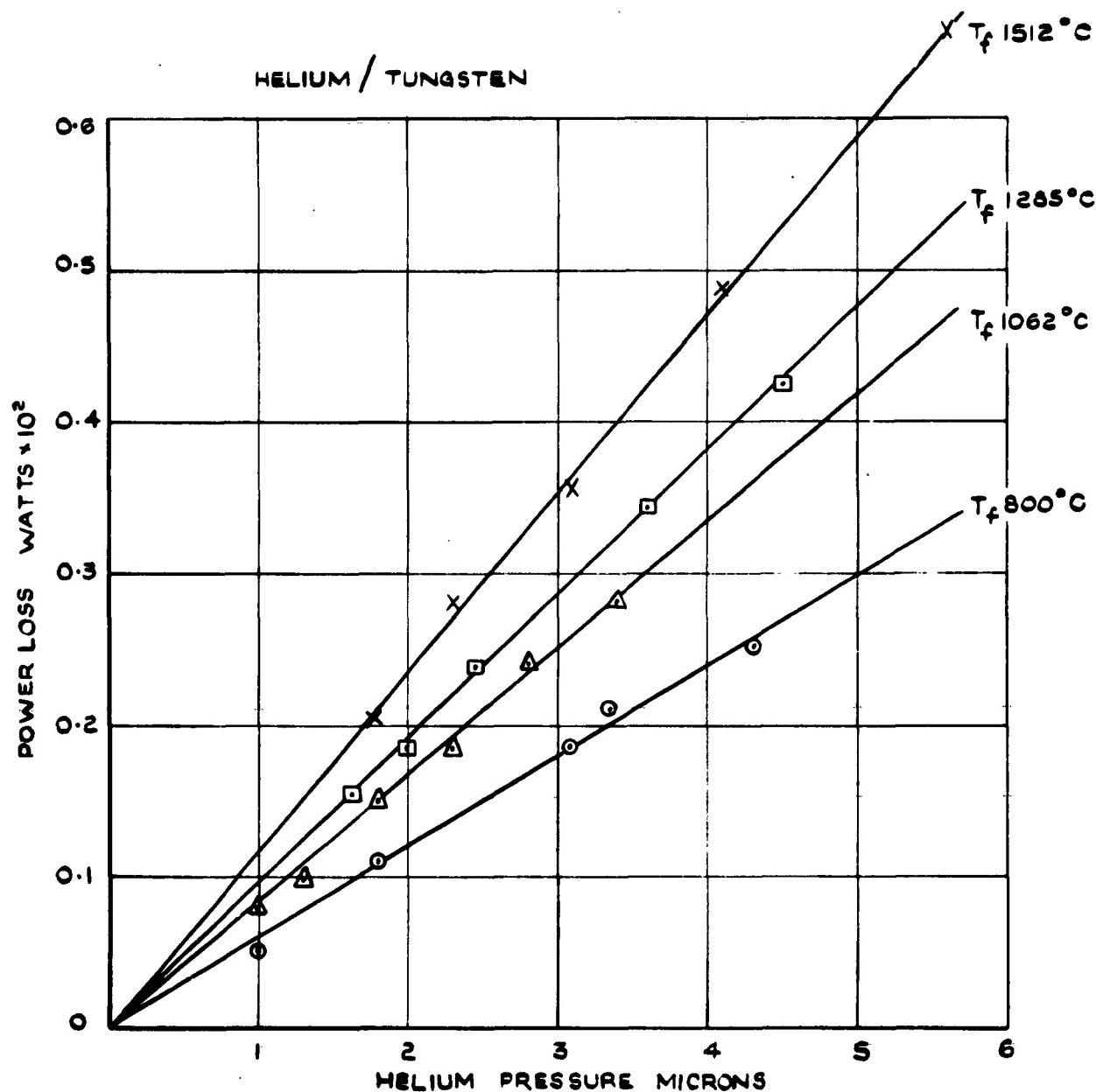


FIG. 7. RELATION BETWEEN POWER LOSS AND GAS PRESSURE FOR HELIUM ON TUNGSTEN AT DIFFERENT FILAMENT TEMPERATURES.

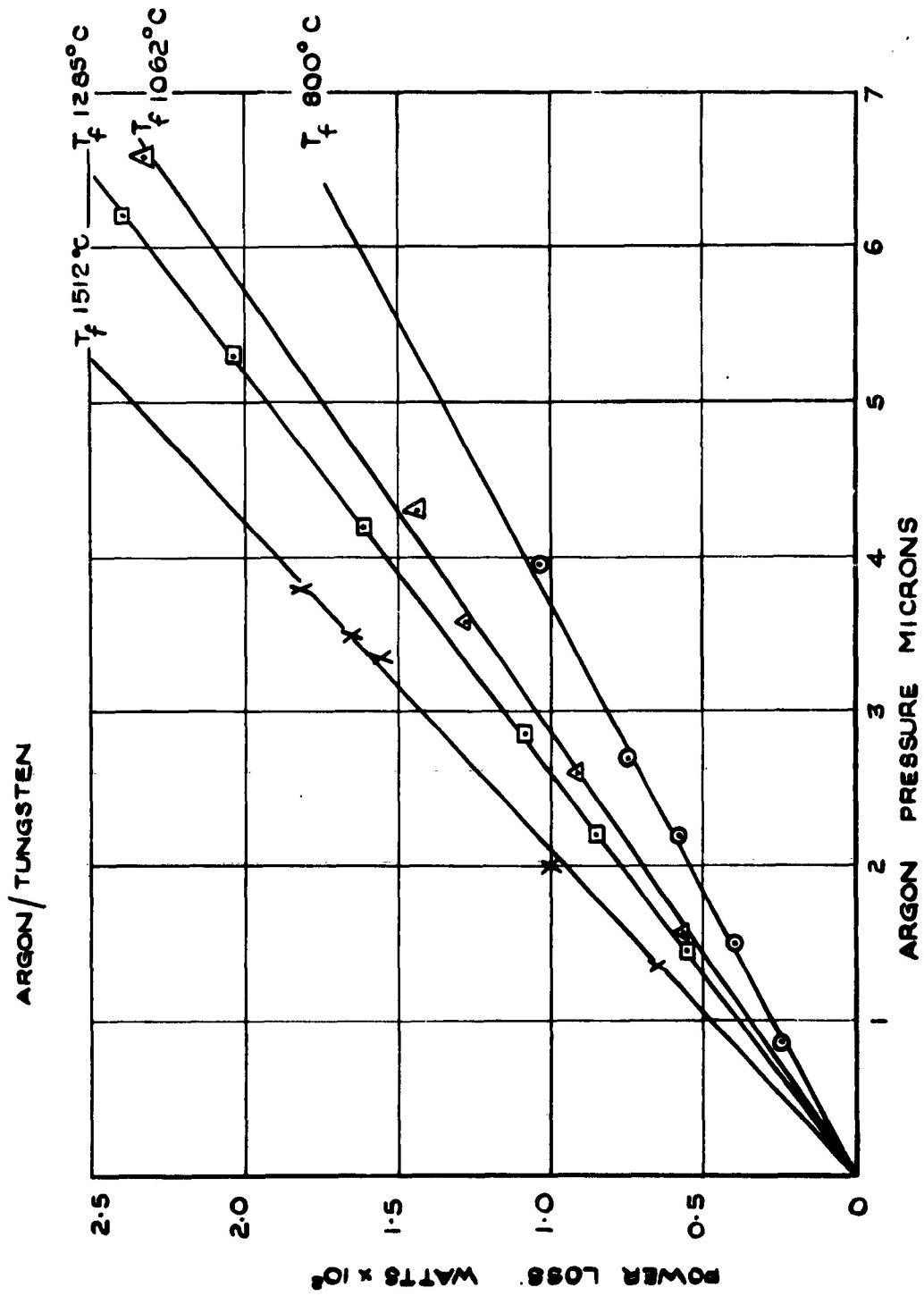


FIG. 8. RELATION BETWEEN POWER LOSS AND GAS PRESSURE FOR ARGON ON TUNGSTEN AT DIFFERENT FILAMENT TEMPERATURES

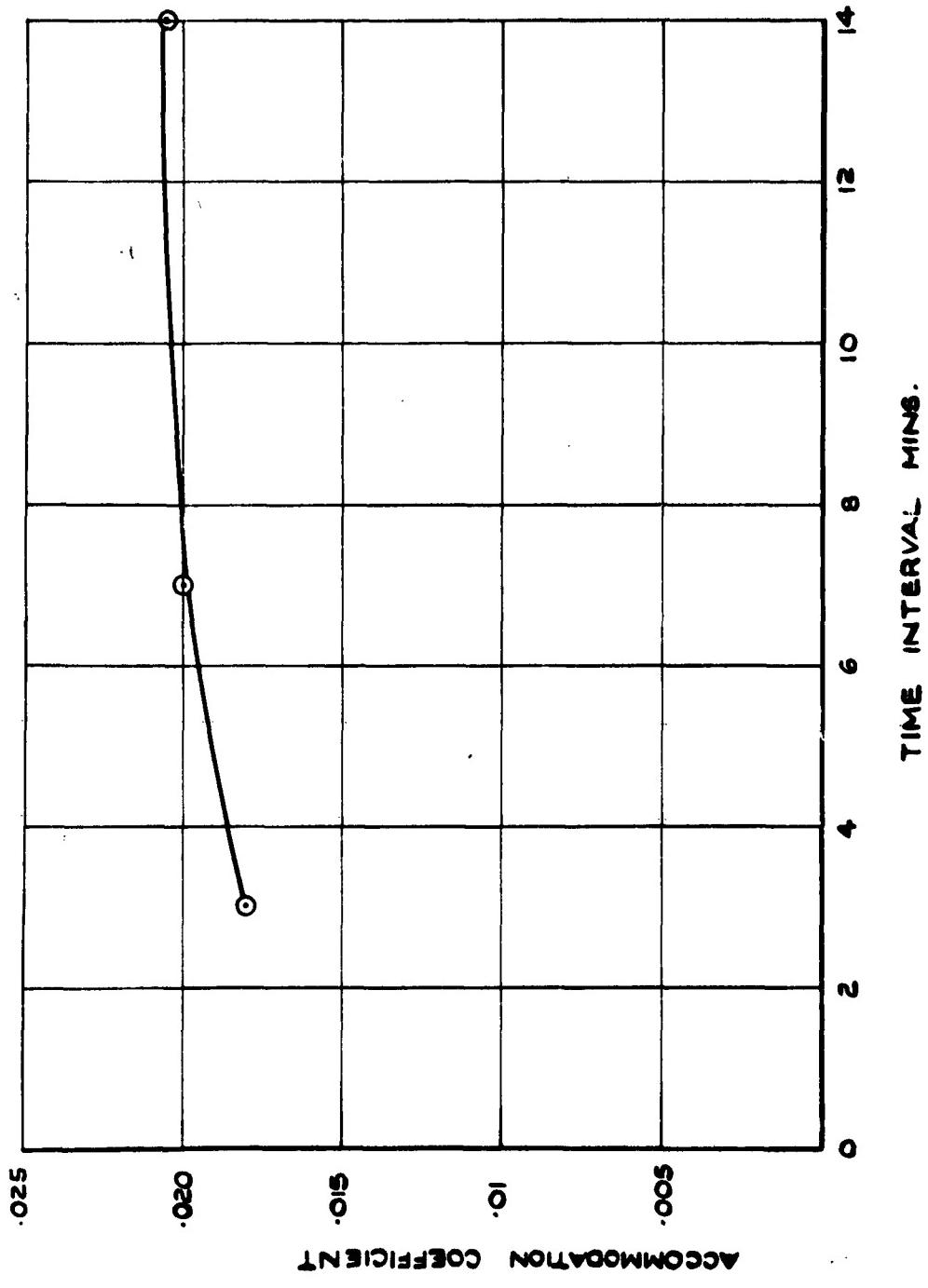


FIG. 9. HELIUM ON TUNGSTEN AT 1062°C . EFFECT OF TIME INTERVAL BETWEEN FLASHING AND ADMISSION OF HELIUM ON ACCOMMODATION COEFFICIENT.

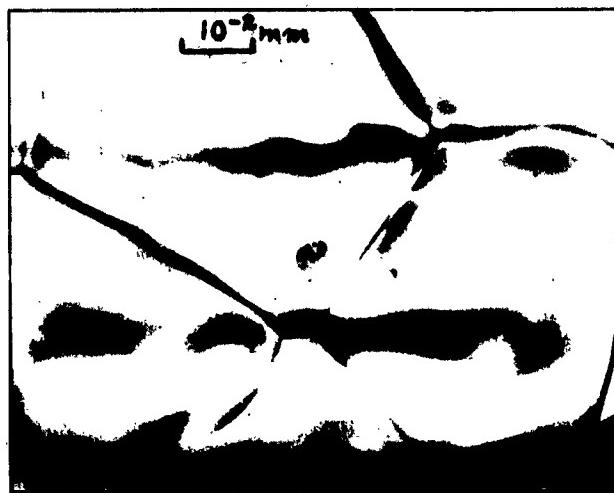


FIG.10.

SURFACE OF TUNGSTEN FILAMENT AFTER
THE EXPERIMENTS SHOWING THERMAL
ETCHING OF GRAIN BOUNDARIES

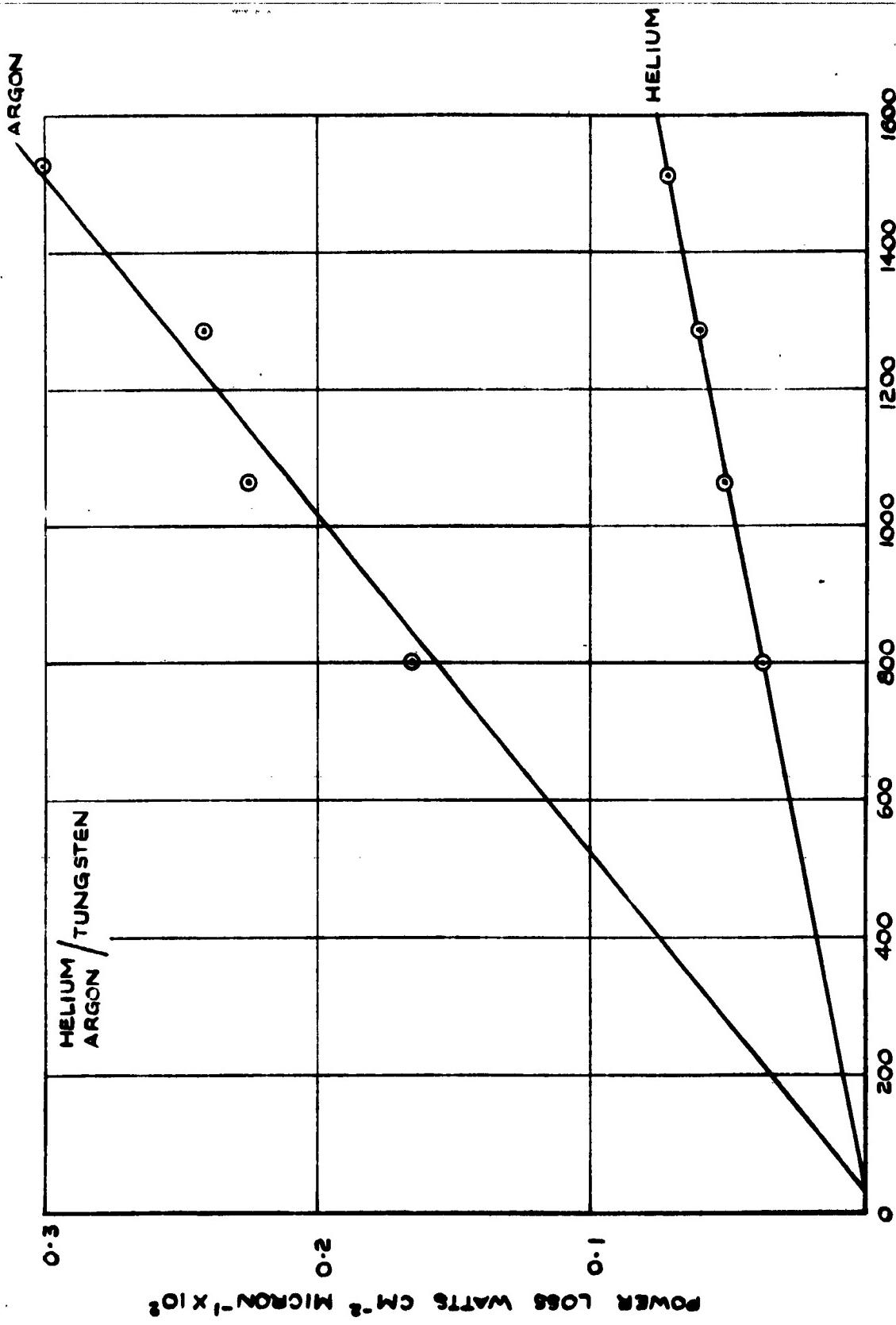


FIG II. RELATION BETWEEN POWER LOSS AND FILAMENT TEMPERATURE FOR HELIUM AND ARGON ON TUNGSTEN.

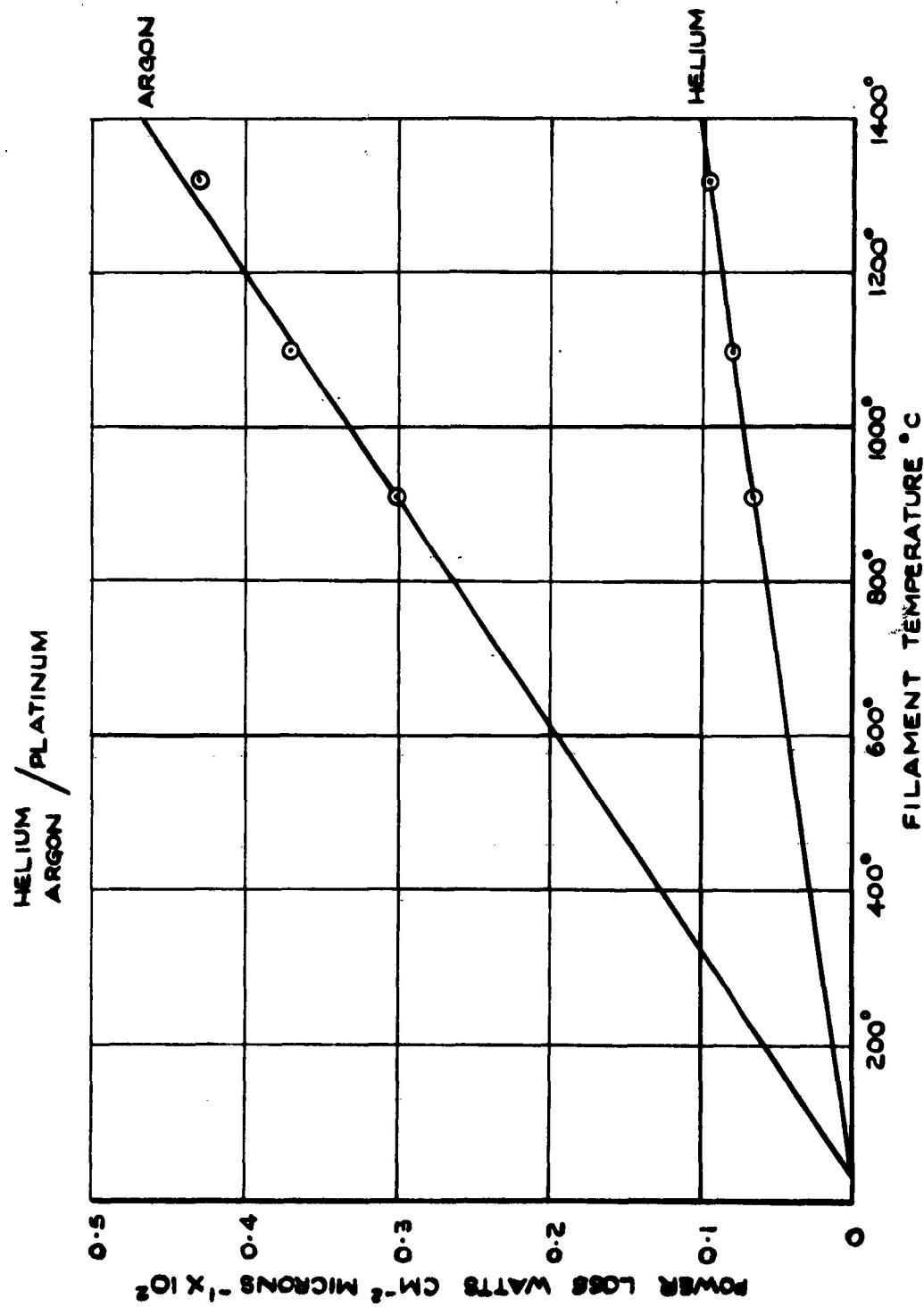


FIG.12. RELATION BETWEEN THE POWER LOSS AND THE FILAMENT TEMPERATURE FOR HELIUM AND ARGON ON PLATINUM AFTER CLEANING IN OXYGEN.

DETACHABLE ABSTRACT CARDS

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THE THERMAL ACCOMMODATION OF HELIUM AND ARGON ON TUNGSTEN AND PLATINUM AT ELEVATED TEMPERATURES. Watt, W. and Morton, R. August 1964.

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An accommodation coefficient of 0.018 for helium on tungsten and of 0.24 for argon, both constant over the temperature range studied, was found. On platinum these gases and also nitrogen had constant accommodation

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